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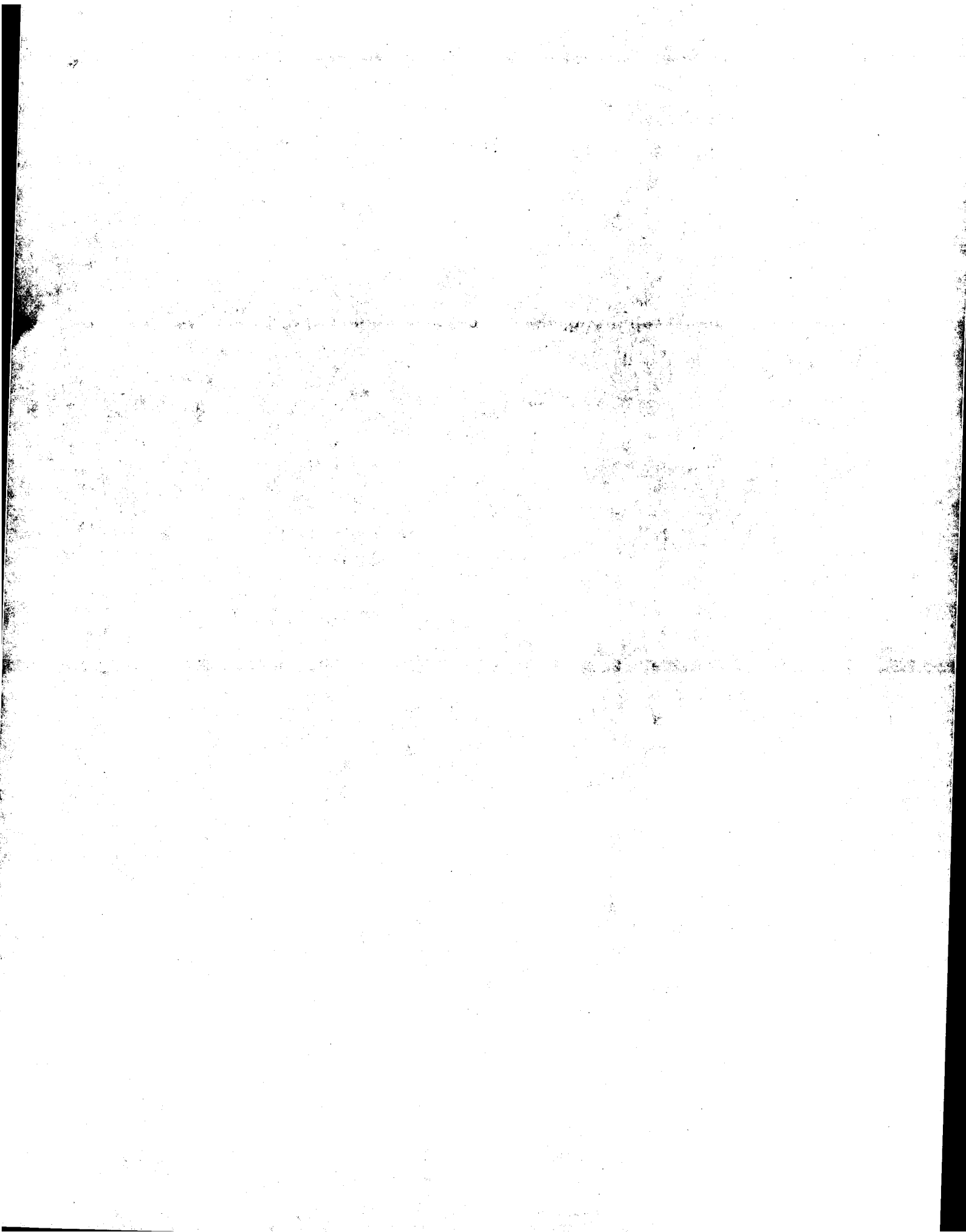
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PATENT SPECIFICATION

NO DRAWINGS

1035,262



Date of Application and filing Complete Specification: April 21, 1964.

No. 16493/64.

Application made in United States of America (No. 274,815) on April 22, 1963.

Complete Specification Published: July 6, 1966.

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Index at acceptance:—C3 Q(C8C, C11, C17, D1A, T2A); C3 P(2C6B, 2C8C, 2C11, 2C14B, 2C17, 2D1A, 2K7, 2T2A).

Int. Cl.:—C 08 c 11/46

COMPLETE SPECIFICATION

Preservation of Diene Rubbers

ERRATA

SPECIFICATION No. 1,035,262

Page 1, line 68, for "inibit" read "inhibit"
 Page 2, line 3, for "dramtic" read "dramatic"
 Page 3, line 9, after "at" insert "a"
 Page 6, line 13, for "between" read "within"
 Page 6, line 14, for "15%" read "1—5%"
 Page 6, line 37, for "atome" read "atoms"

THE PATENT OFFICE
 1st January 1969

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change resulting from variations in polymerization, cross-linking and continued polymerization. Styrene-butadiene copolymer rubber (SBR) is made by emulsion polymerization and the rubber is first obtained in latex form. The antidegradant is normally added to the latex in which the external phase is water but must find its way into the organic rubber phase. Dispersibility and ability to penetrate the rubber are required, for which properties liquid form is desirable. Low water solubility and conversely high solubility in the rubber phase are vital in order to achieve quantitative or near quantitative incorporation into the rubber upon coagulation of the latex. Coagulation is normally effected by acidic salt solution and therefore the antidegradant must be stable to acid and possess low solubility in the aqueous acid medium.

Absence of toxicity is another important requirement. During processing the rubber comes into contact with the operators and frequently the finished rubber article comes

synthetic rubbers which do not much exposure cracking or are not stable enough to withstand the vulcanization process. It is an object of the present invention to provide effective substantially non-toxic preservatives which can be incorporated into the rubber at completion of the manufacture to preserve the unvulcanized rubber, and which carry over their activity into the vulcanized product to reduce the inhibit exposure cracking and aging.

It has long been recognised that N-alkyl-N'-phenyl-p-phenylenediamines inhibit the aging of natural rubber. More recently, it was found that N-isopropyl-N'-phenyl-p-phenylene-diamine inhibits exposure cracking of synthetic rubber vulcanizates and this compound has come into considerable commercial use for this purpose. However, it is a skin sensitizer and volatile enough to cause numerous cases of skin eruption among workers processing the rubber. Moreover, it is much too soluble in the aqueous coagulating medium used for SBR to be considered for protecting

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SEE ERRATA SLIP ATTACHED

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COMPLETE SPECIFICATION

Preservation of Diene Rubbers

We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis, 66, State of Missouri, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preservation of diene rubbers and to compositions containing such rubbers together with preserving agents therefor, herein referred to as antidegradants.

An acceptable rubber antidegradant must meet a variety of requirements. Incorporation presents special problems. Whereas natural rubber latex is protected by natural antioxidants, it is necessary to add a preservative to synthetic diene rubbers as soon as they are formed. They must be protected from change resulting from oxidation, de-polymerization, cross-linking and continued polymerization. Styrene-butadiene copolymer rubber (SBR) is made by emulsion polymerization and the rubber is first obtained in latex form. The antidegradant is normally added to the latex in which the external phase is water but must find its way into the organic rubber phase. Dispersibility and ability to penetrate the rubber are required, for which properties liquid form is desirable. Low water solubility and conversely high solubility in the rubber phase are vital in order to achieve quantitative or near quantitative incorporation into the rubber upon coagulation of the latex. Coagulation is normally effected by acidic salt solution and therefore the antidegradant must be stable to acid and possess low solubility in the aqueous acid medium.

Absence of toxicity is another important requirement. During processing the rubber comes into contact with the operators and frequently the finished rubber article comes

into contact with the user. The presence of toxic ingredients in the rubber is therefore most undesirable. Low volatility is important both to avoid toxic effects and prevent loss of protection. Rapid mixing, vital to mass production techniques, causes high processing temperatures and some antidegradants when present in the hot rubber have caused severe skin burns and irritation from exposure to the vapors. Similarly, volatility of the antidegradant results in lowering the service life of the rubber article and staining of light coloured articles in contact with rubber containing it.

There is a demand for antidegradants which prevent aging due to absorption of oxygen from the atmosphere and prevent exposure cracking due to ozone. The problem of exposure cracking is especially acute with synthetic rubbers because vulcanizates thereof are more susceptible to this type of degradation than natural rubber vulcanizates. Most adjuvants now used to preserve unvulcanized synthetic rubbers either do not inhibit exposure cracking or are not stable enough to withstand the vulcanization process. It is an object of the present invention to provide effective substantially non-toxic preservatives which can be incorporated into the rubber at completion of the manufacture to preserve the unvulcanized rubber, and which carry over their activity into the vulcanized product to reduce the inhibit exposure cracking and aging.

It has long been recognised that N-alkyl-N'-phenyl-p-phenylenediamines inhibit the aging of natural rubber. More recently, it was found that N-isopropyl-N'-phenyl-p-phenylene-diamine inhibits exposure cracking of synthetic rubber vulcanizates and this compound has come into considerable commercial use for this purpose. However, it is a skin sensitizer and volatile enough to cause numerous cases of skin eruption among workers processing the rubber. Moreover, it is much too soluble in the aqueous coagulating medium used for SBR to be considered for protecting

SEE ERRATA SLIP ATTACHED

unvulcanized SBR.

- 5 It has now been discovered that there is a dramatic disappearance of toxicity if the alkyl substituents contain six or seven carbon atoms. Whereas N - sec. - butyl - N'-phenyl-*p*-phenylenediamine is comparable to the corresponding N-isopropyl compound in its toxicity, toxicity completely disappears upon replacing the lower secondary alkyl groups with the secondary alkyl groups containing six or seven carbon atoms. Tests of various rubber formulations on fifty human subjects have demonstrated that the compounds were neither primary irritants nor skin burning agents. These chemicals did not produce any sensitization in the fifty humans tested.

15 Dermatitis effects were studied on a series of N - alkyl - N'-phenyl-*p*-phenylenediamines

where the alkyl group varied from 3 to 8 carbon atoms. Ten human volunteer subjects who had been previously sensitized to N-sec. butyl - N' - phenyl-*p* - phenylenediamine were used in evaluating each chemical. A rubber sample containing the test chemical was applied to the skin of the volunteers for 24 hours. The rubber samples were then removed and the maximum reactions during the 72-hour period after removal were noted and recorded. Numerical rating were assigned and recorded on a scale of 0-4 where higher numbers indicated increasing severity of reaction and then reassigned on the basis of weighted rating as follows in order to express the data on a scale of 0-100, on which the blank rubber stock containing no added chemical was 100:

Rating	Weighted Rating	
0	10	No reaction
1	8	Very slight reddening
2	6	Definite reddening with slight swelling
3	4	Severe reddening and severe swelling
4	2	Weeping blister and severe reddening

- 40 A zero rating was observed on all of the ten subjects for the rubber containing no added chemical. Accordingly, multiplying the weighted rating (10) by the ten subjects in that category provided an overall rating of 100 for the blank stock. The number of persons

assigned to each of the five categories, after being exposed to rubber containing a chemical was multiplied by the weighted rating for that category and the results totalled to provide an overall rating for the chemical. The results follow :

Alkyl Radical	Overall Toxicity Rating on Basis of Blank as 100
isopropyl	56
sec. butyl	61
sec. amyl	67
sec. hexyl	94
sec. heptyl	88
sec. octyl	71

- 50 According to the present invention, therefore, there is provided a composition comprising a vulcanizable diene rubber having incorporated therein, as an antidegradant and in an amount sufficient to reduce degradation, an N - alkyl - N' - phenyl-*p*-phenylenediamine, wherein the said alkyl substituent is a secondary alkyl group containing 6 or 7 carbon atoms.

As referred to later herein the vulcanizable diene rubber may be a synthetic vulcanizable diene hydrocarbon or a natural rubber or a mixture of such.

The antidegradants just set forth enter essentially quantitatively into the rubber phase of SBR rubber. This may be shown by tests conducted to determine the ability of the anti-

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5 degradants to enter an organic phase. Thus, tests were made by adding antidegradant in amount of 1% by weight of the benzene to a mixture of 5 ml. of benzene and 100 ml. of aqueous hydrochloric acid salt solution. One salt solution used had pH about the middle of the range normally encountered in commercial operations and an-

other was at pH slightly below that range. The mixtures were vigorously shaken until equilibrium was reached and the partition between the aqueous and organic phases determined. Results were as follows where the figures recorded are percent of the antidegradant in the aqueous phase.

Antidegradant	% In Aqueous Phase	
	pH 1.75	pH 3
N-sec.-Butyl-N'-phenyl- <i>p</i> -phenylene-diamine	83	33.2
N-sec.-Hexyl-N'-phenyl- <i>p</i> -phenylene-diamine	22.5	4.3

20 It is apparent that at a pH of 3 essentially all of the N-sec.-hexyl-N'-phenyl-*p*-phenylenediamine enters the organic phase. The presence of this compound in unvulcanized styrene-butadiene copolymer rubber preserves the rubber from cross-linking and hardening during storage and processing.

25 The antidegradants used in the present invention are obtainable from readily available raw materials by well known production techniques. They may be prepared for example by reductive alkylation of *p*-nitro or *p*-aminodiphenylamine with methylethyl ketone, 2-octanone or methylisoamyl ketone

30 Examples are

N-(1, 3-dimethylbutyl)-N'-phenyl-*p*-phenylenediamine.

N-(1, 4-dimethylpentyl)-N'-phenyl-*p*-phenylenediamine.

35 N-(1, 3-dimethylpentyl)-N'-phenyl-*p*-phenylenediamine.

N-(1-methylpentyl)-N'-phenyl-*p*-phenylenediamine.

40 They are emulsifiable liquid products stable enough to withstand vulcanization temperatures. Although normally obtained as liquids they can be induced to crystallise to low-melting solids on standing with appropriate seeding.

45 The resistance to degradation of SBR by ozone imparted by the new antidegradants is similar to that imparted by the toxic lower homologues although there is a decline in potency as the series is ascended and the effect soon becomes insignificant. While 50 N-(1, 3-dimethylbutyl)-N'-phenyl-*p*-phenylenediamine consistently exhibited 90% or more of the antiozonant effectiveness of lower homologues, compounds containing 55 eight carbon atoms in the secondary alkyl groups were only two-thirds as effective. Introduction of alkyl into the other nitrogen substituent of the aforesaid compound was even more detrimental. For example N-(1, 3-dimethylbutyl)-N'-*p*-tolyl-*p*-phenylenediamine 60 was only about 70 percent as effective in resisting ozone under static conditions. To demonstrate this, anti-exposure cracking tests were conducted by the stress relaxation method for measuring ozone cracking described by 65 Decker and Wise in *Rubber World*, April 1962, pages 66-69. Accelerated tests were performed in an ozone chamber under dynamic conditions in order to simulate conditions 70 encountered in service.

The following Examples will serve to illustrate the invention :—

Example 1

The test stock comprised:

Parts by Weight

SBR 1500 rubber	100.
Carbon black (HAF)	50.
Zinc oxide	4.
Stearic acid	2.
Hydrocarbon softener	10.
N.-tert. Butyl 2-benzothiazolesulfenamide	1.
Sulfur	1.75
Antidegradant	1.5

5 SBR 1500 rubber is styrene-butadiene
 copolymer rubber made at 41°F., the bound
 styrene content of which is 23.5%. The
 stocks so compounded were cured in the usual
 manner by heating in a press at 144°C. and
 the optimum cures alternately stretched and
 relaxed on a reciprocating mechanism which
 imparted 25% strain to the test pieces 90
 10 times each minute in an atmosphere which
 contained approximately 25 parts O₃ per
 hundred million. The extent of cracking in
 a test piece was determined by measuring the

forces required to extend the test pieces 100%
 before and after exposure to ozone. As the
 strips began to crack the number of stress
 supporting rubber chains decreased and the
 force required to extend the strip 100% was
 reduced. The ratio of this force to the
 original force was calculated and the ability
 of the rubber to resist ozone cracking was
 obtained by a comparison of these numbers.
 These ratios are referred to as percent of the
 original modulus.

Antidegradant	Hours to Indicated Percent of Original Modulus		
	70%	80%	90%
None	9	6	3
N-sec.-Butyl-N'-phenyl- <i>p</i> - phenylenediamine	37	26	14
N-(1,3-Dimethylbutyl)-N'-phenyl- <i>p</i> -phenylenediamine	33	23	12
N-(1,4-Dimethylpentyl)-N'-phenyl- <i>p</i> -phenylenediamine	31	22	11
N-(1-Ethyl-3-methylpentyl)-N'- phenyl- <i>p</i> -phenylenediamine	29	20	10

EXAMPLE 2

As further illustrative of the invention, exposure cracking tests were carried out with a mixture of synthetic polybutadiene rubber

and natural rubber. The synthetic polybutadiene contained approximately 50% *cis*-polybutadiene. The formulation comprised:

	<i>Parts by Weight</i>
Smoked sheets	50
Polybutadiene (Diene Rubber)	50
Carbon black (HAF)	50
Zinc oxide	3
Stearic acid	2.6
Aromatic processing oil	15
Sulphur	2.4
<i>N-tert.</i> -Butyl-2-benzothiazolesulphenamide	0.5
Antidegradant	2.0

The formulations were vulcanized in the usual manner and the vulcanized products aged 48 hours at 100°C. in circulating air.

Anti-exposure cracking tests by the stress relaxation method were then carried out as described above.

<u>Antidegradant</u>	<u>Hours to Indicated Percent of Original Modulus</u>		
	<u>70%</u>	<u>80%</u>	<u>90%</u>
None	13	7	3
N-Isopropyl-N'-phenyl- <i>p</i> -phenylenediamine	30	19	9
N-(1,3-Dimethylbutyl)-N'-phenyl- <i>p</i> -phenylenediamine	33	21	10

EXAMPLE 3

To illustrate preservation of unvulcanized polybutadiene a 6% polybutadiene toluene cement (hydrocarbon >90% *cis*) was used. Antidegradant (0.5% of the rubber hydrocarbon) was dissolved in the cement and the toluene removed by steam distillation. The

wet ball of elastomer was collected and dried by milling at 105°C. for 5 minutes. The rolls were then chilled to 20-25°C. and the rubber sheeted out thinly. Viscosity change after aging at 100°C. in a circulating air oven was followed by means of a Mooney plastometer.

<u>Antidegradant</u>	<u>Mooney Plasticity after Aging</u>			
	<u>0 Hrs.</u>	<u>16 Hrs.</u>	<u>24 Hrs.</u>	<u>48 Hrs.</u>
N-Isopropyl-N'-phenyl- <i>p</i> -phenylene-diamine	38	44	45	48
N-(1,3-Dimethylbutyl)-N'-phenyl- <i>p</i> -phenylenediamine	38	47	51	60

The unprotected composition cannot even be evaluated. It disintegrates to crumbs during drying.

In general, the compounds used in this invention are particularly valuable for the preservation of sulphur vulcanizable diene rubbers especially those unsaturated rubbers containing more than 50% diene hydrocarbon. This group of preferred rubbers includes natural rubber, styrene-butadiene copolymer rubber and the various stereo specific polymerized dienes, for example, *cis*-polybutadiene and *cis*-polyisoprene. The amount to use will vary, depending upon the particular formulation and the purpose of the compounder,

but in general will fall between the range of 0.15% of the rubber content. The stereo specific rubbers are normally obtained as cements and it is preferred to add the antidegradant to the cement immediately after polymerization has been completed. These rubbers deteriorate rapidly unless adequately protected.

EXAMPLE 4

Protection of the natural rubbers was demonstrated in formulation comprising :

Parts by Weight

Smoked sheets	100
Carbon black (HAF)	50
Zinc acid	5
Stearic acid	3
Saturated hydrocarbon softener	3
Sulphur	2.5
N- <i>tert.</i> -Butyl-2-benzothiazole sulfenamide	0.5
Antidegradant	1.5

The formulations were vulcanized in a press in the usual manner by heating 45 minutes at 144°C. The vulcanizates were then artificially aged by heating for 72 hours in a circulating air oven at 100°C. and for 7 days in a bomb under 300 pounds oxygen pressure

per square inch. The percentage of the original tensile retained after aging was determined. The vulcanizates were also flexed at 25°C. in an atmosphere containing 25 ± 5 parts of ozone per 100 million parts of air until a crack appeared.

Antidegradant	% Tensile Retained After Aging		Ozone Resistance
	100°C. in air	70°C. in oxygen	Hrs. Until Cracked
None	10	0	12
N-(1,3-Dimethyl butyl)-N'-phenyl- <i>p</i> -phenylenediamine	53	47	72
N-(1-Isobutyl-3-methyl-butyl)N'-phenyl- <i>p</i> -phenylenediamine	45	42	60

It will be noted that increasing the number of carbon atoms in the alkyl chain reduced the effectiveness.

Of course, admixtures of the antidegradants can be used and are in some cases preferred. The presence of more than one ingredient lowers the melting point and reduces possibility of crystallization. Although the products are normally obtained as liquids, N-(1,3-

dimethylbutyl)-N'-phenyl-*p*-phenylenediamine can be induced to crystallize to a low melting solid (m.p. 33°C.) on standing with appropriate seeding.

WHAT WE CLAIM IS :—

1. A composition comprising a vulcanizable diene rubber having incorporated therein, as an antidegradant and in an amount suffi-

cient to reduce degradation, an N-alkyl-N'-phenyl-*p*-phenyl-enediamine, wherein the said alkyl substituent is a secondary group containing 6 or 7 carbon atoms.

5 2. A composition according to claim 1 wherein the antidegradant is N-(1,3-dimethyl-butyl)-N'-phenyl-*p*-phenylenediamine.

10 3. A composition according to claim 1 wherein the antidegradant is N-(1,4-dimethyl-pentyl)-N'-phenyl-*p*-phenylenediamine.

4. A composition according to any claims 1-3 wherein the rubber comprises natural rubber.

15 5. A composition according to any of the claims 1-3 wherein the rubber comprises a synthetic hydrocarbon rubber.

6. A composition according to claim 5 wherein the rubber comprises a styrene-butadiene copolymer rubber.

20 7. A composition according to claim 6 wherein the rubber comprises a latex of styrene-butadiene copolymer rubber.

25 8. A composition according to any claims of 1-3 wherein the rubber comprises polybutadiene rubber.

9. A composition according to any of claims 1-8 which contains both natural rubber

and a synthetic diene rubber.

10. A composition according to any of claims 1-9 wherein the antidegradant is present in the composition in a proportion of 0.1 to 5% of the rubber present. 30

11. A composition according to claim 1 substantially as hereinbefore described with reference to any of the foregoing specific Examples 1 to 4. 35

12. A composition according to any of claims 1-10 in which the rubber is vulcanized.

13. A process for reducing the tendency to degradation of a vulcanizable diene rubber which comprises incorporating therein, in an amount sufficient to reduce degradation, an N - alkyl - N' - phenyl - *p* - phenylenediamine, wherein the said alkyl substituent is a secondary group containing 6 or 7 carbon atoms. 40

14. A process according to claim 13 substantially as hereinbefore described. 45

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